RESEARCH ON LOW DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000°F

Fourth Quarterly Status Report
Contract NASr-99
National Beryllia Corporation
Haskell, New Jersey

RESEARCH ON LOW DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000°F

Summary Status Report
For the Period Jan. 1, 1963 to March 31, 1963

This summary status report supplements the attached copy of the paper, "Low Density Thermal Insulation Materials for Use Above 3000°F" presented orally at the Ceramic Materials for Nuclear Power and Space Applications Symposium, American Ceramic Society, 65th Annual Meeting, Pittsburgh, Pennsylvania, April 30, 1963.

Matrix Materials - The higher purity zirconia raw material (700 ppm total impurities) referred to in the paper tends to produce a more dense fired foam ceramic than previously used. It exhibits better refractoriness but poorer thermal shock resistance. Variations in foaming technique and setting agents are being examined in order to produce a matrix of better physical properties. To insure that adequate foamed ceramic will be available for tests to 4000°F, additional efforts are being directed towards higher purity magnesia and improved setting agents for thoria so that foams of these materials may be considered as alternates to zirconia.

Composites - Preliminary thermal conductivity data for zirconia foam Zr6 alone and with both continuous and discontinuous phases

of graphite added are presented in the paper. The difference in the slopes of the thermal conductivity verses temperature curves indicates that the continuous phase of two component composite governs the curve slope. Moreover, it is encouraging to note that neither of these specimens display the marked upturn in conductivity apparent in the foam matrix above about 2400°C. The higher purity zirconia, when perfected, will be similarly impregnated and tested to the higher temperatures which will be available shortly.

Efforts are continuing in attempts to produce uniform foams containing hollow spheres of zirconia coated with a thin film of metallic tungsten.

A method has been developed for the fabrication of stabilized zirconia foams which have incorporated in them aromatic hydrocarbons. The nature of the decomposition during inert firing and the disposition of the residue during the high temperature treatment are being evaluated and compared for four types of aromatic hydrocarbons.

Thermal Transfer Cell

Design and engineering for the conversion of the thermal transfer cell from a refractory metal heater to a graphite helix heater have been completed. Components are being fabricated and procured in preparation for final assembly. This modification will increase the temperature capabilities of the cell to the point where hot face temperatures of the specimen of 4500°F will be obtainable. Thermal conductivity curves may then be extended

about 4000°F on those materials and composites which will withstand this temperature. Trial runs for thermal conductivity measurement on the modified apparatus are scheduled to begin June 10, 1963.

RESEARCH ON LOW DENSITY THERMAL INSULATION MATERIALS FOR USE ABOVE 3000°F

By - Karsten H. Styhr
Philip S. Hessinger
Dr. Eugene Ryshkewitch

National Beryllia Corporation
Haskell, New Jersey

There are many insulation materials available for thermal protection with various densities, chemical compositions and degrees of refractoriness. There are, however, very few and possibly no materials which can combine low density with good thermal insulating properties in the temperature range above 3000°F. The reason behind this is, of course, that foam structures while having good thermal resistivity at low temperatures, rapidly deteriorate above 2400°F due to the transfer of heat through the pores by thermal radiation. The increase in these radiation or photon heat transfer effects with temperature being proportional to the third power of temperature, cause a drastic loss in thermal protection in the higher temperature ranges.

Figure 1 illustrates typical thermal conductivity vs. temperature curves for some of the more common ceramic oxides. It may be noted that most of these materials exhibit a decrease in thermal conductivity with increasing temperature to some point above 2000°F. Only silica and zirconia, one of the best thermal insulators in its dense form, show an increase in thermal conductivity from room temperature upwards.

Figure 2 compares measured values for a dense alumina ceramic and a calculated curve for a 50% dense alumina foam, this K_f being predicted for the foam as a result of the conductivity component K_c and the radiation component K_r as shown in the

NATIONAL BERYLLIA CORPORATION

THERMAL CONDUCTIVITY OF DENSE CERAMIC INSULATION AS A FUNCTION OF TEMPERATURE

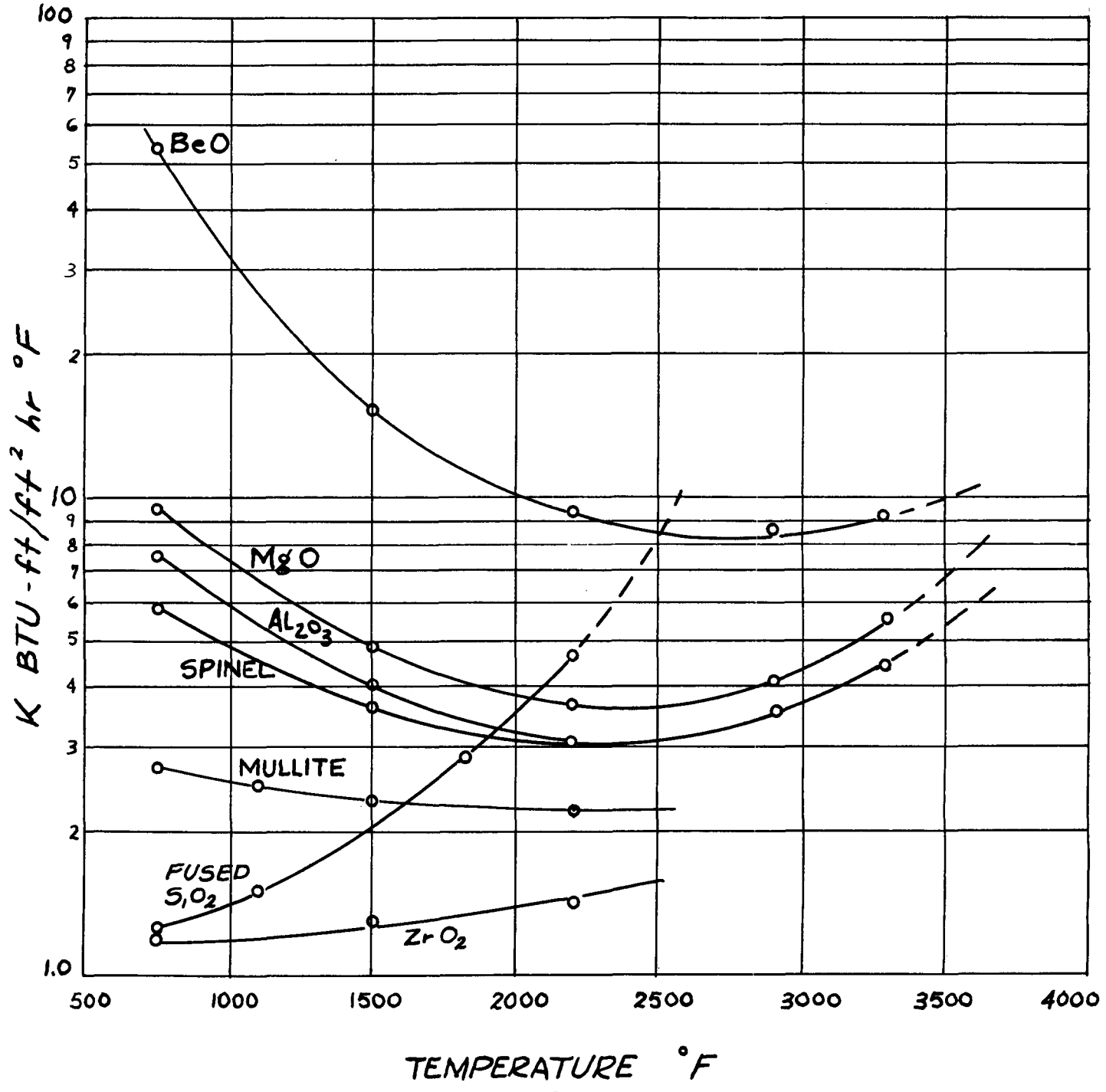


FIGURE 1

NATIONAL BERYLLIA CORPORATION

THERMAL CONDUCTIVITY OF AL_2O_3 FOAM INSULATION

CALCULATED, ASSUMING

K_C = CONDUCTION COMPONENT

K_R = RADIATION COMPONENT = $4 \gamma d e \sigma T^3$

WHERE $\gamma = 2/3$ FOR SPHERICAL PORES

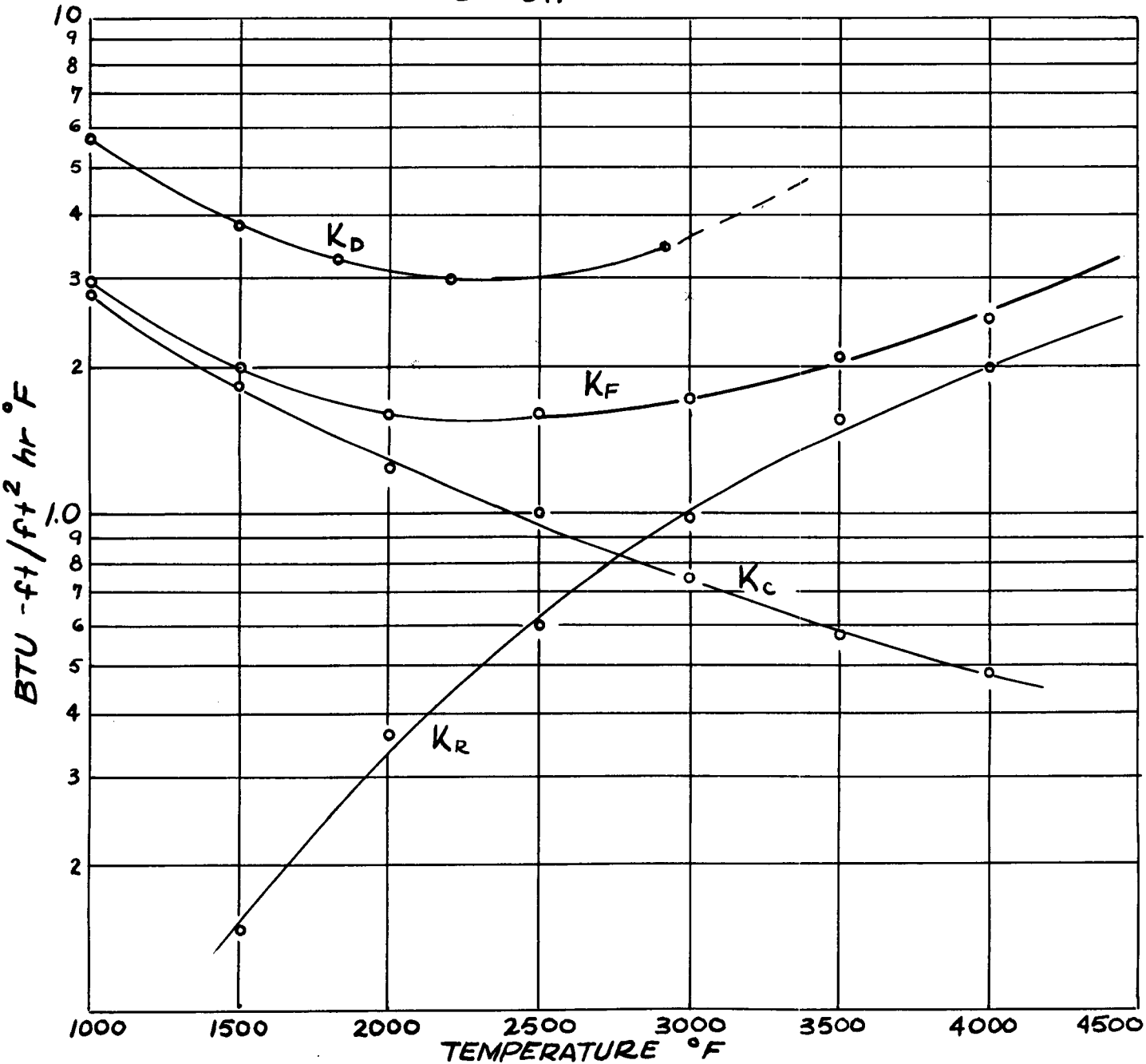
d = 3MM (ASSUMED)

σ = CONSTANT 1.4×10^{-12} CAL/SEC/CM^2/DEG^4

T = TEMP. ABSOLUTE

e = 0.1

FIGURE 2



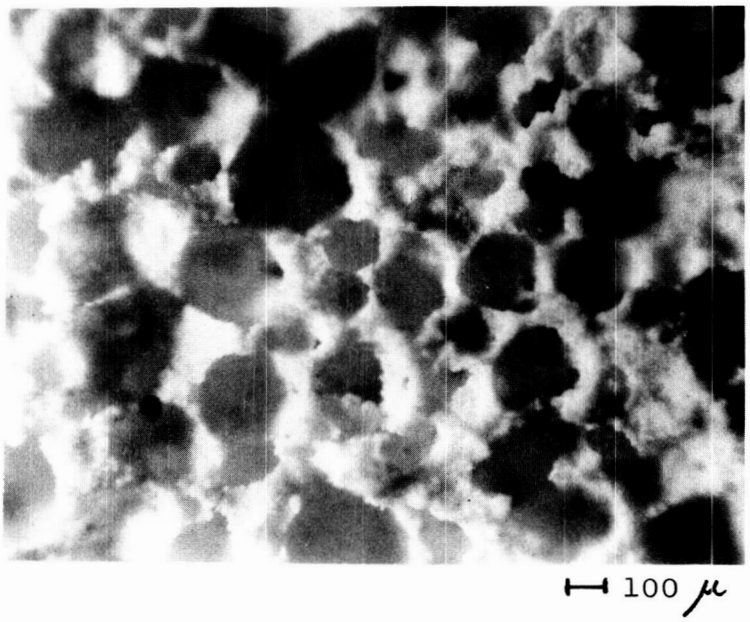


FIGURE 3

99.9% PURE THORIA FOAM(50X)

equation at the top. It may be seen that this thermal radiation component becomes dominant at temperatures above about 2400°F. It is the goal of this research program to find a means of retarding this photon contribution to the total or apparent thermal conductivity.

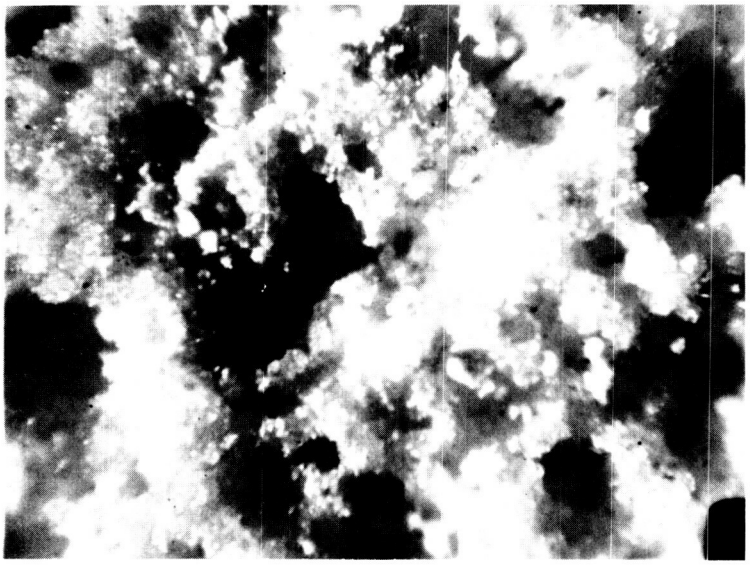
The method employed is to introduce into each individual cell of a ceramic foam or cellular type of structure, a material which will disperse at high temperatures to form a radiation barrier and thus retard heat transfer. Mechanisms such as: (1) absorption and re-radiation by imbedded particles of high emissivity characteristics, (2) scattering of thermal energy by incorporated phases of optimum size and mean free path characteristics, and (3) reflection by metallic foil radiation barriers, were considered and are being examined.

Before a concept such as the one proposed may be evaluated a ceramic foam matrix must be available which will withstand temperatures in the range of interest, that is above 3000°F. Alumina, silica, mullite, spinel, and zircon were considered and then eliminated because of their borderline refractory characteristics. Thorium oxide with a melting point of 5910°F is a good possibility because of its low inherent thermal conductivity. Sample foams were prepared of this material for preliminary evaluation and to determine feasibility. Typical microstructure of thorium oxide foams is shown at 50X in Figure 3. Unfortunately, this oxide

also inherently has a high density with a specific gravity of over 10. Foams which were 80 to 85% porous after firing to 3000°F had typical specific gravity values of 1.2 to 2.0 g/cc, considered somewhat high for possible applications. For this reason we went on to examine other materials.

Beryllia also a good refractory oxide with a melting point of 4650°F is attractive because of its low density with the specific gravity of 3.008. It, however, is noted for its high thermal conductivity and was therefore relegated to be considered only in the later stages of the program.

Magnesium oxide with a melting point of over 5000°F and exhibiting reasonably low values for both specific gravity and thermal conductivity was considered more fully. High purity MgO raw materials are somewhat of a problem in that they are scarce and relatively expensive when you are looking for the third or fourth nine in percent purity. An available commercial grade of MgO, about 99% pure, was fabricated into a foam structure however, with a density of about .80 g/cc. Figure 4 shows the microstructure at 50X of such a magnesia foam ceramic. All preliminary measurements were promising, however, in the measurement of thermal conductivity of specimens of foamed magnesia, the tendency of extreme grain growth in the direction of the thermal gradient was noted. Actual zone refining or the diffusion of trace impurities along the temperature gradient was detectable by both X-ray and spectrographic methods in those portions of the



⊢ 100 μ

FIGURE 4

HIGH PURITY MAGNESIA FOAM(50X)

specimen subjected to temperatures above 3000°F. The traces of calcia and boron present in the raw material became concentrated in the cooler portions of the sample as tri-calcium borate leaving a radial, fibrous structure in the hotter portions, relatively free of these impurities.

Zirconium dioxide with a melting point of 4700°F was also considered in the early stages of this investigation. As mentioned earlier it has extremely low thermal conductivity even its dense form and its specific gravity of 5.6 is not unreasonably high. Quite pure raw materials may be obtained at reasonable cost and although zirconia does have a crystallographic inversion from the monoclinic form to a cubic form at high temperature, the oxide may be stabilized in this latter form by the formation of a solid solution of zirconia with small amounts of such oxides as calcia, yttria and others. Excellent zirconia foams have been fabricated by a variety of techniques. Figure 5 shows the microstructure of one such zirconia foam at a magnification of 50X. Such foams of stabilized zirconium oxide have been prepared at densities from about .6 to 1.5 g/cc. One procedure was selected which produces .85 to .90 g/cc material after firing to 3000°F and specimens prepared for treatment by a variety of methods.

One group of zirconia foams was impregnated with an essentially continuous phase of pyrolytic graphite. This was done in order to raise the emissivity of zirconia from its normal value

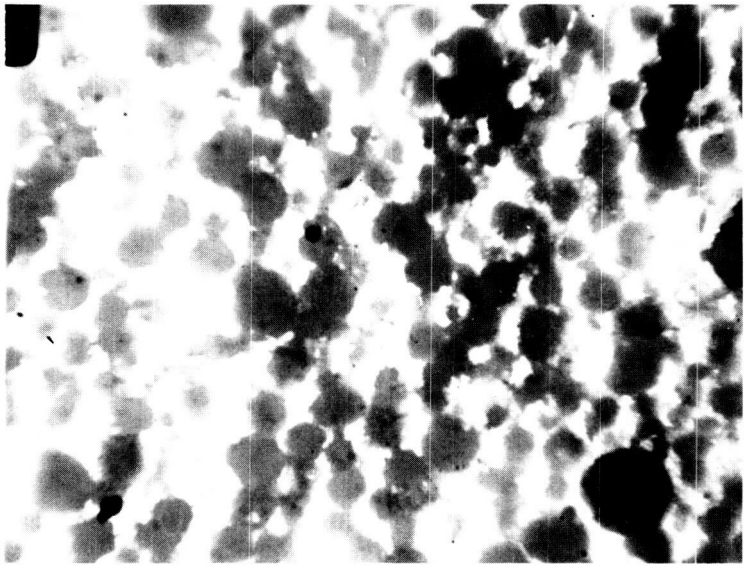


FIGURE 5

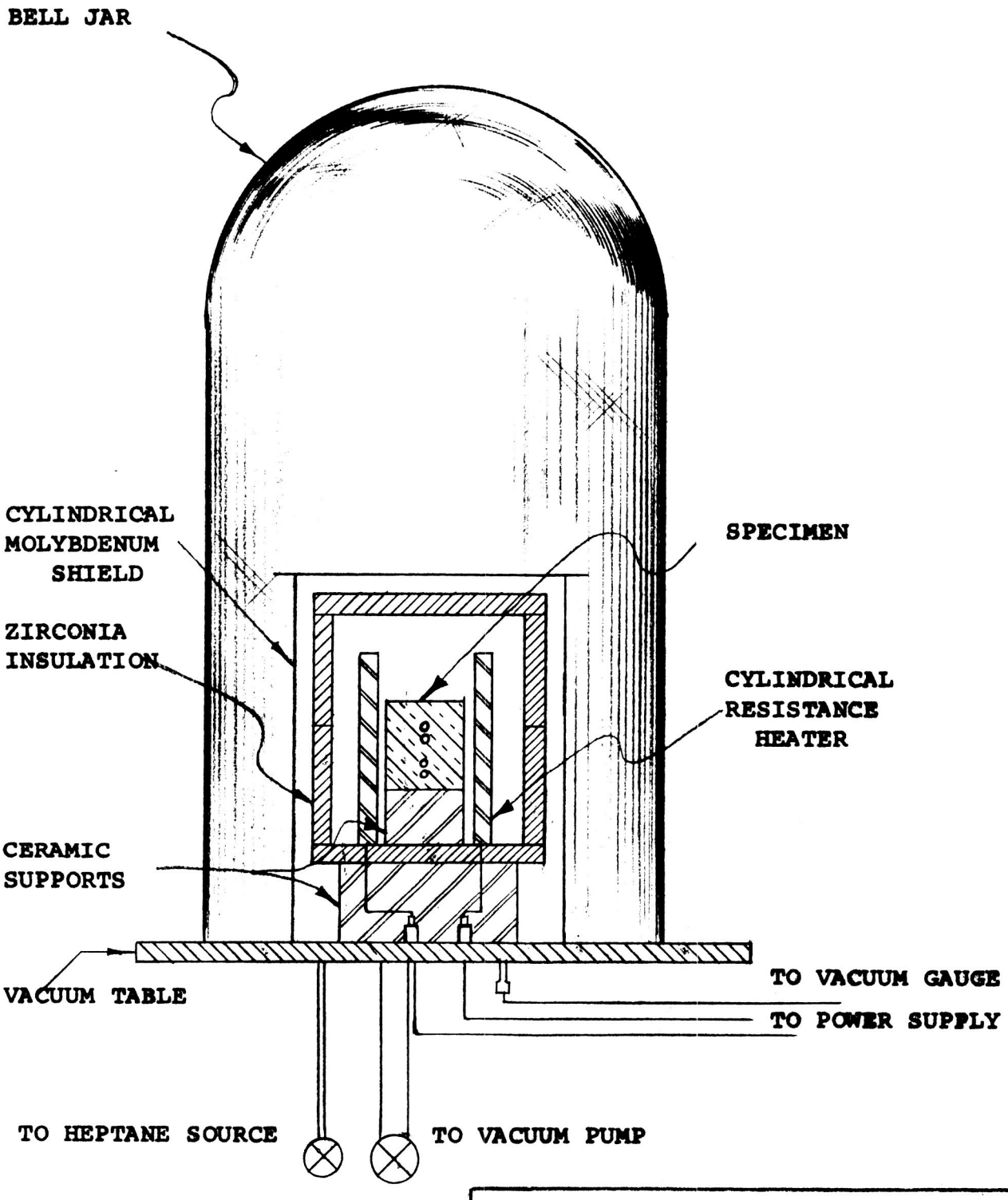
STABILIZED ZIRCONIA FOAM(50X)

of about .3 to that of unity. It was accomplished by placing the fired zirconia specimens in a vacuum bell jar (Figure 6) and evacuating to a pressure of about 10 microns. At this point the bell jar was isolated from the vacuum pump and the chamber back-filled with heptane vapor to a pressure of approximately 4 millimeters of mercury by controlling the temperature of liquid heptane in an adjacent vessel. The specimen when heated to about 1000°C in this atmosphere was coated on all surfaces exposed to the heptane vapor with a thin layer of pyrolytic graphite.

Another method used to obtain an essentially continuous phase of graphite on all surfaces of a zirconia foam specimen was by vacuum impregnation of a colloidal graphite suspension. Figure 7 is a photomicrograph of such a zirconia foam with an essentially continuous phase of graphite on the surface of the zirconia.

Zirconia foams were also prepared in which the graphite is essentially made a discontinuous phase. This was accomplished by incorporating graphite particles of a descrete size range during the foaming operation. Figure 8 shows the microstructure of such a zirconium oxide carbon composite. Firing, of course, must be done in an inert or reducing atmosphere to prevent oxidation of the carbon during firing.

Carboneous deposites may also be introduced within the foam structure by the incorporation of insoluable aromatic hydrocarbons during the foaming operation.



NATIONAL BERYLLIA CORP.

PYROLYTIC DEPOSITION CHAMBER

FIGURE 6

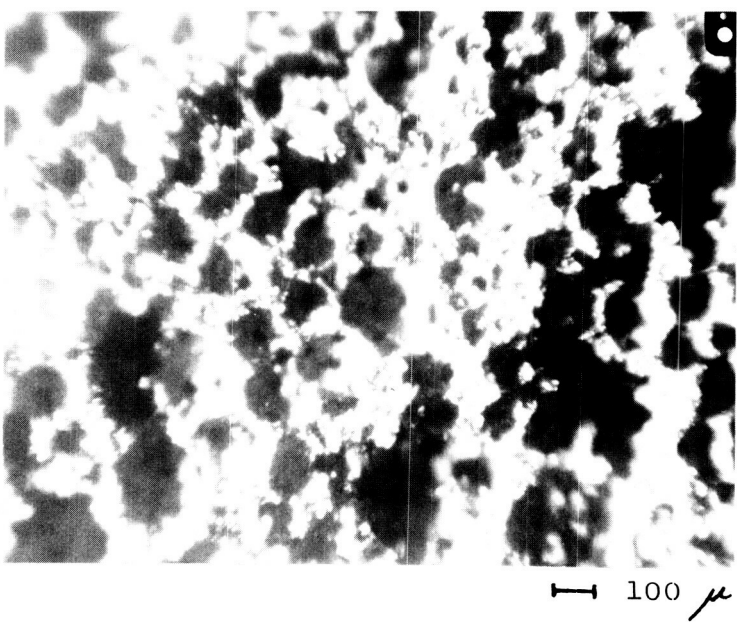


FIGURE 7

ZIRCONIA FOAM WITH CONTINUOUS
PHASE FOR COLLOIDAL GRAPHITE

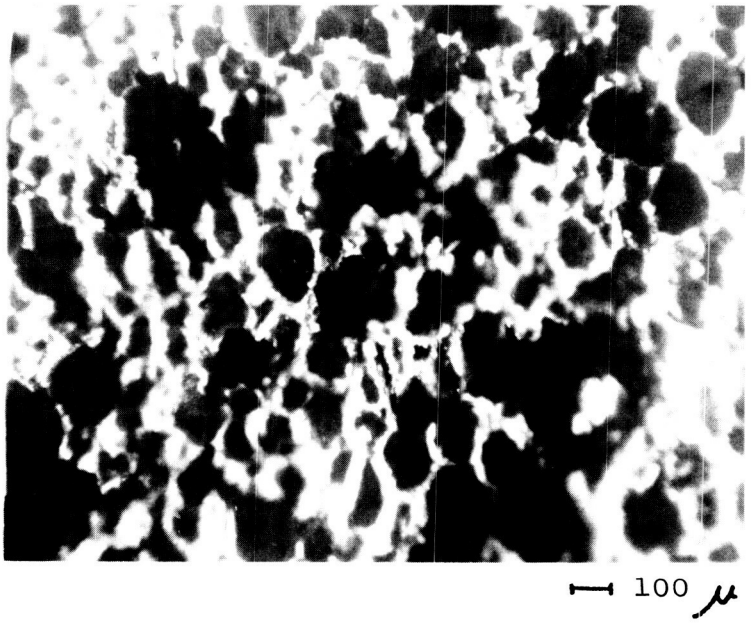


FIGURE 8

ZIRCONIA FOAM WITH DISCONTINUOUS
PHASE OF GRAPHITE

Another approach to the reduction of the radiation component of thermal conductivity at high temperatures is to introduce metallic foil heat reflectors as a radiation barrier phase. Small hollow microspheres of zirconia have been obtained and coated with a thin layer of metallic tungsten by a pyrolytic vapor deposition method. Such coated particles may be introduced into the foam during the foaming operation and, after drying the composite, fired in an inert or reducing atmosphere. It is also possible to vapor deposit an oxidation resistant coating over the tungsten by another gas phase reaction leaving a coating of alumina, beryllia or other oxide ceramics as desired.

The method of measurement of thermal conductivity of these ceramic foams and composite specimens should next be considered briefly. Essentially we designed and built a direct rather than a comparative type of instrument which uses the steady state, radial heat flow method. Our specimen is a right circular cylinder 2" in diameter and of infinite length (infinite length in this case being 9"). Normally we stack a series of three or more specimens to form this cylinder. Figure 9 is a schematic of the geometry of our device. The heater, as we have used it to date, is of tungsten or molybdenum wire wound on a dense beryllia muffle and placed inside of a dense beryllia thermocouple protection tube. The cylindrical specimen, with a 3/4" I.D. central hole is placed over the heater so that all heat must pass through the specimen in a radial direction. End losses are minimized to

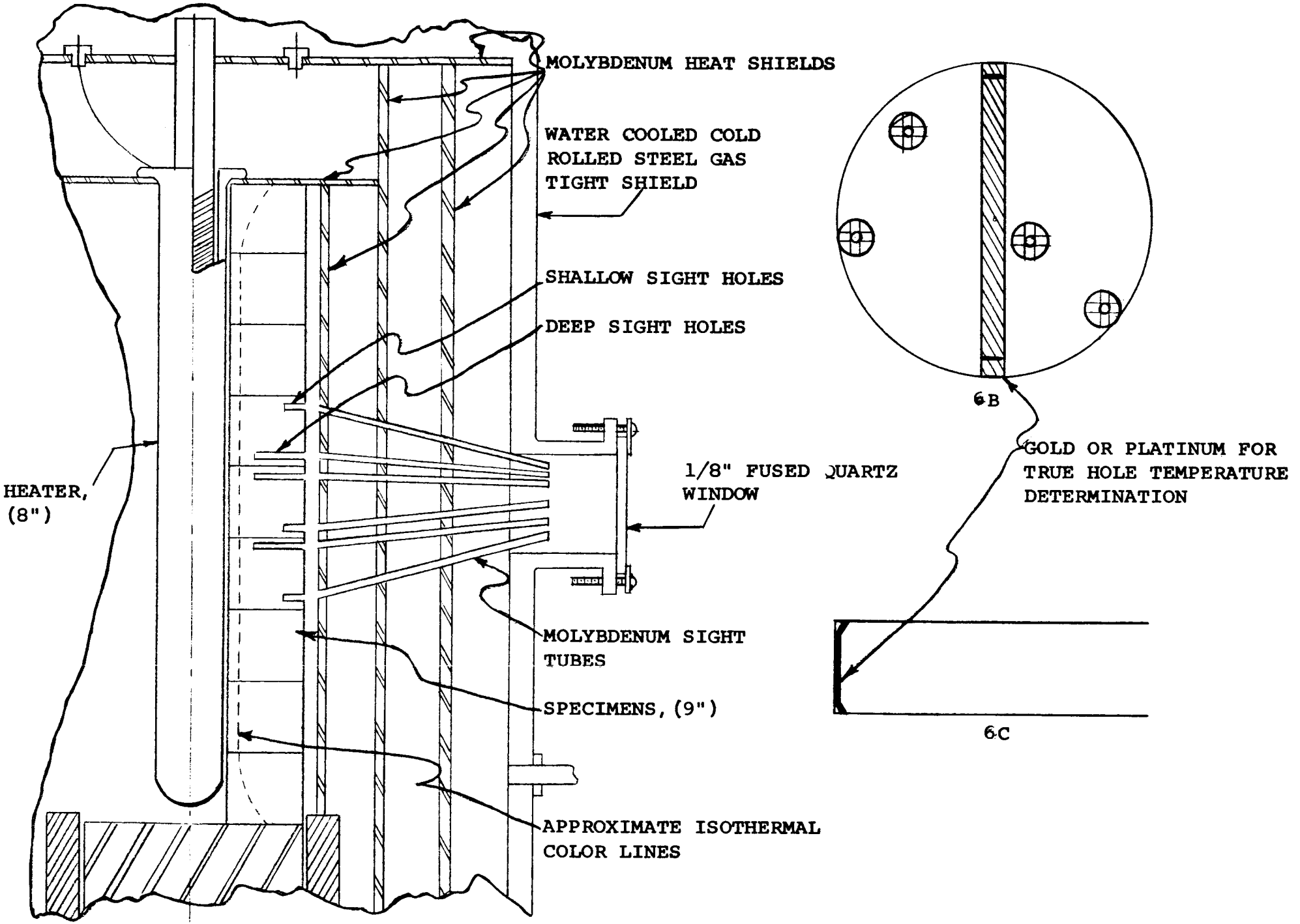


FIGURE 9 Schematic of Sight Hole Geometry

some extent by insulation and radiation shielding. Calculations are made for the 1" long central section of the specimen so that 4" on each end of the specimen function as guard rings.

The radial temperature gradient is measured by drilling holes of two accurately known depths from the outer periphery of the specimen. Refractory metal sight tubes are provided from the fused quartz window in the water cooled steel outer jacket. Temperatures are measured over a 3" length in the center to insure that radial heat flow has truly been established. In operation only small random temperature differences are noted in holes of equal depth over the central 3" length. In addition, isothermal color lines are visible within the specimens after measurement. These are normally examined after a run to substantiate that radial heat flow had been accomplished during the measurement. A typical profile of an isothermal color line is shown in the dotted line through the specimen in Figure 9.

It may be noted in this figure that there is no thermal insulation other than the molybdenum radiation shields and of course the specimens themselves. Under steady state conditions with a heater temperature of 3600^{o}F and a "hot face" temperature (in the deeper of the sight holes) of 3250^{o}F the outer molybdenum radiation shield typically measures 800^{o}F and adequate cooling of the exterior steel shell is achieved at a water flow rate of about .2 to .3 gallons per minute.

Temperatures are measured by several methods. Initial work and the data presented at this time were measured by an infrared radiation pyrometer and a "hot wire" optical pyrometer. Initially we were concerned with the emittance characteristics of the sight holes. Holes of various depths and relatively low length to depth ratios in composite materials of varying emissivity are not ideal conditions under which to assume black body conditions. For this reason we measured the emittance at the bottom of several holes in each type of specimen. This was accomplished by placing small strips of pure gold and then pure platinum along the isotherms in the bottoms of both shallow and deep sight holes as shown in Figure 9, and actually observing their melting.

Figure 10 shows data points for normal spectral emittance in the 1.5 to 2.6 micron response range of our infrared pyrometer at the melting points of gold and of platinum in the deep and shallow holes. Also shown is a total normal emittance measurement in inert atmosphere on a specimen of dense zirconia reported by the Southern Research Institute. A first approximation of emittance correction for our sight holes of depths indicated can then be made by drawing a curve of the approximate shape of the SRI curve through the two data points obtained at the melting points of gold and platinum. Infrared pyrometer readings corrected in this manner have yielded smooth experimental curves in good agreement with published thermal conductivity data on materials of similar composition, properties and structure.

△ = Normal Spectral (1.5 to 2.6μ) emittance in hole of length to depth ratio of 1 drilled into dense zirconia (hydrogen 25 V/O nitrogen atmosphere)

○ = Normal Spectral (1.5 to 2.6μ) emittance in hole of length to depth ratio of 4 drilled into dense zirconia (hydrogen 25 V/O nitrogen atmosphere)

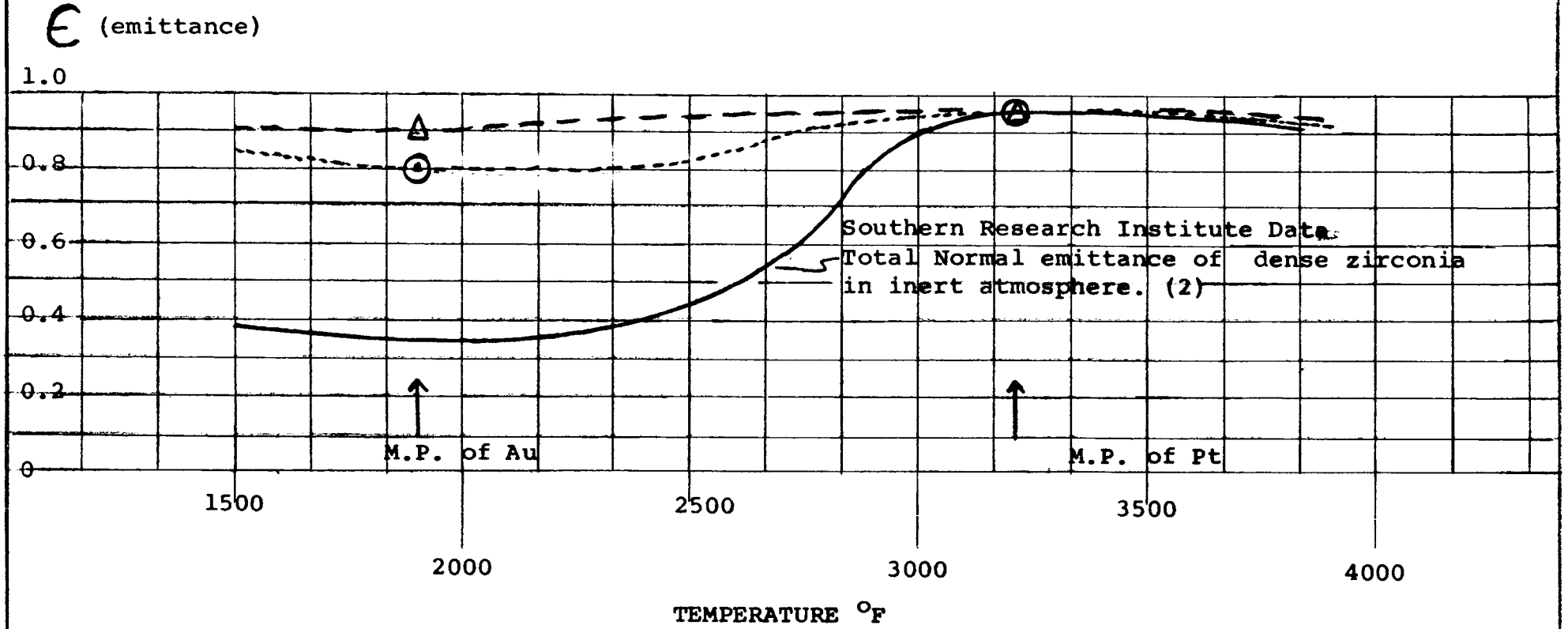


Figure 10
Emittance Correction for Holes of Selected L/D in Dense Zirconia

Thermal conductivity may be calculated under steady state conditions by determining the heat flow "q" passing through the specimen, that is, the power input, and the temperature gradient over a known distance. The equation used is:

$$K = \frac{q \ln \frac{(r1)}{(r2)}}{2\pi L \Delta T}$$

The only other measurements are the ratio of the radii of the bottoms of the two sight holes, assumed to be the same at measurement temperatures as that easily measured at room temperature and the length of the specimen which is radially heated. Since our primary concern was for a valid comparative rather than absolute data this experimentally simple apparatus was considered adequate in spite of the number of sources of error involved.

Figure 11 is a photograph of some typical specimens. It may be noted in the center of this photograph three sections which together form a 9" zirconia foam specimen. The section intact at the left was the top, in the center, split in half, is the central section and on the right, also cut apart to expose the isothermal color lines, the bottom most portion of the specimen. It is apparent in examining the cross-section of these pieces that the isothermal color lines are indeed obvious and can be used to substantiate the assumption that radial heat flow conditions were established. In the left foreground of the photo is a section of magnesia foam. Close examination will reveal that the

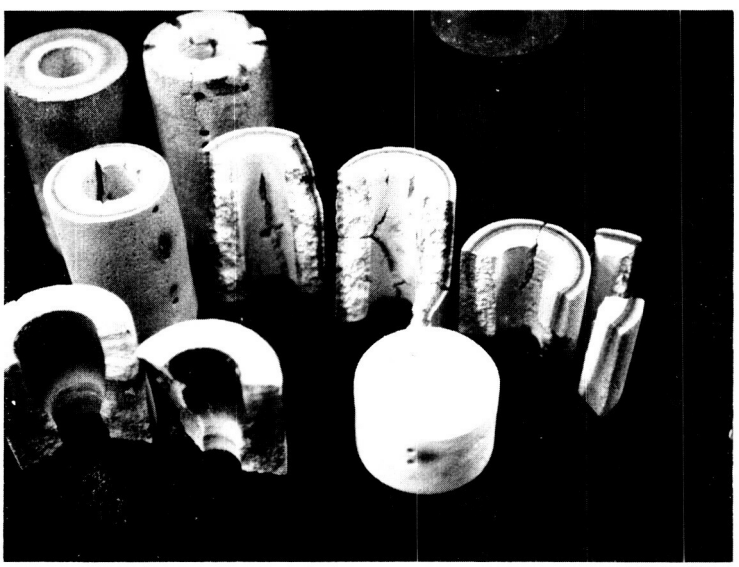


FIGURE 11

FOAMED CERAMIC SPECIMENS
AFTER CONDUCTIVITY MEASUREMENT

internal area, of course, the hottest part of the specimen, has indeed been greatly affected and shows extreme grain growth and severe shrinkage.

Figure 12 shows thermal conductivity vs. temperature curves measured on our apparatus along with some accepted published data. Our first few runs, made for equipment calibration purposes, were made on a 99.5% pure alumina of 92% of theoretical density. These points, measured only with an optical pyrometer, are in fair agreement with some MIT data measured on material of a similar purity and density. Since alumina was not considered refractory enough for our application no further data points were considered necessary after a premature termination of this measurement run.

Next we measured an 8% calcia stabilized zirconia sintered to 85% of theoretical density. These were measured with the optical pyrometer as indicated by the dark circles and later with the infrared pyrometer corrected for emittance as previously described. Shown also are MIT data on a dense zirconia and some Southern Research Institute Data on several samples of dense zirconia. You will note we very comfortable fall right in the middle of these fairly widely differing values. Also shown is the thermal conductivity curve for a 15% calcia stabilized zirconia foam having a density of about 55 pounds per cubic foot or roughly 15% of theoretical.

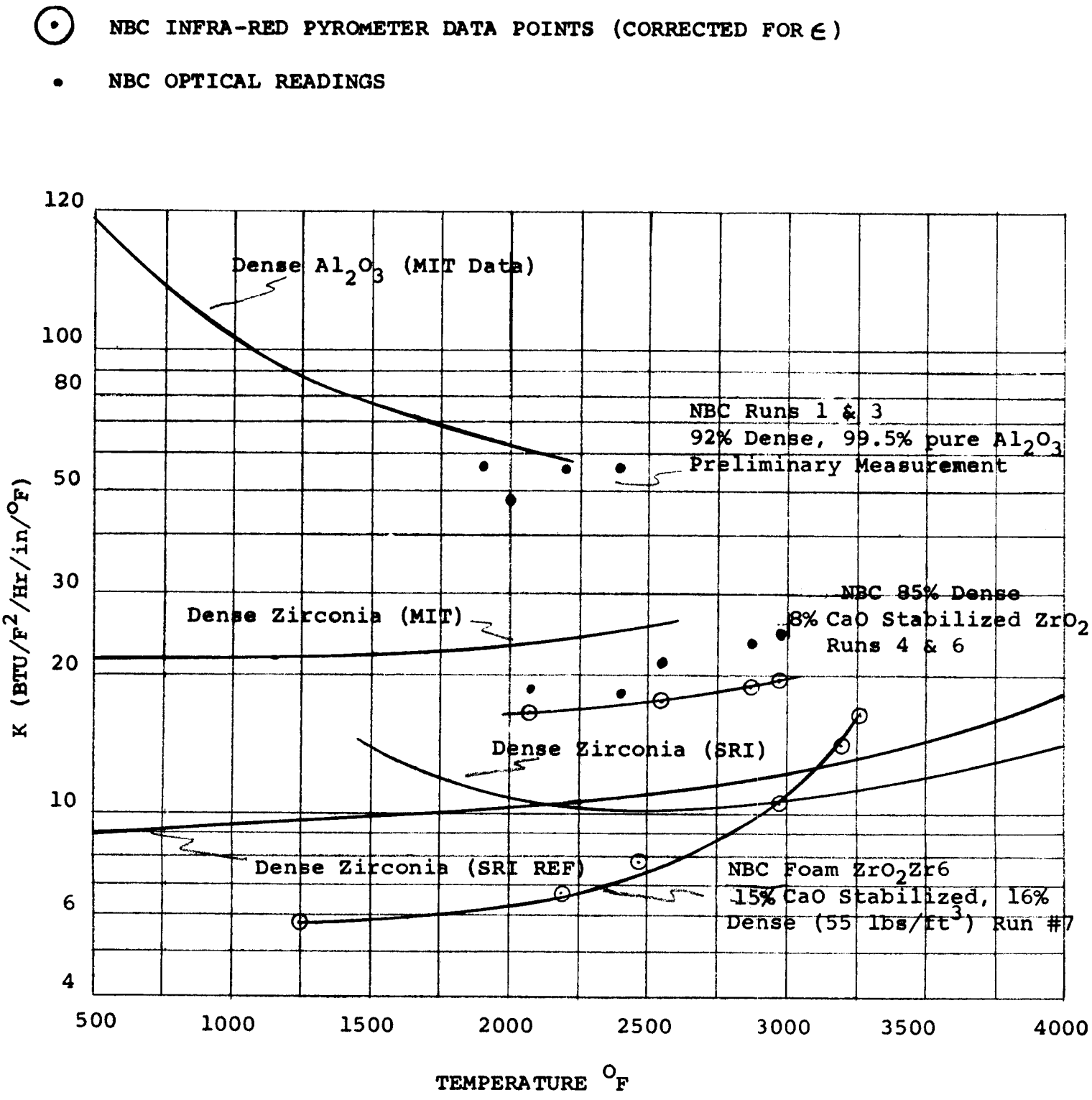


Figure 12
Thermal Conductivity Verses Temperature

In comparing our measurements on the two types of zirconias, it is apparent that the conductivity of the denser one increases about 10%, from around 18 BTU/ft^2/sec./in/$^\circ$F at 2000°F to a value of about 20 at 3000°F. In this same temperature range the foam increases almost 100% from about 6 to 12 BTU/ft^2/sec./in/$^\circ$F, a factor of 10 greater increase in conductivity with temperature. While extrapolation of the curves is not justifiable, it is possible that the two curves may cross at about 3500°F. This foam specimen did show some degradation of the I.D. surface at an estimated temperature of 3450°F, which may account for part of the increase. Starting material for that foam incidently was a C.P. monoclinic zirconia with about 8600 ppm total impurities. We have since gone to a more pure raw material with about 700 ppm impurities and see less of the surface degradation.

Figure 13 shows a few data points on foams treated in different ways in efforts to cut down on the radiation components of thermal conductivity. The bottom one is of course the zirconia foam matrix similar to the curve of Figure 12. This same type of foam was impregnated with graphite by two different methods. One was a physical incorporation of graphite particles screened to between 100 and 200 mesh, yielding a discontinuous added phase. The other is essentially a continuous graphite phase in which a colloidal suspension was vacuum impregnated into the zirconia foam after it had been fabricated and fired. There is an indication of a

difference in slope between the conductivity curves of these two materials and it is interesting to compare them to the curve of a typical graphite shown by the dotted line. It may be noted that the slope of the zirconia foam with the continuous graphite phase approaches that of the graphite itself while the other foam more closely follows the curve of the matrix.

It may be obvious that most data points are only up to 3000°F with only a few runs making measurements to 3250°F. I might add also that these are not mean temperatures but rather the temperatures of the hottest side of the gradient that is measured. This is not, however, the hottest portion in the sample, for the I.D. surface facing the heater would be considerably hotter than that of the deepest sight hole. The reason for this measurement limitation is that we found a temperature limitation in the wire wound, BeO supported heating element at about 3800 - 4000°F at the points where the BeO and refractory metal were in contact.

We have redesigned and are now assembling the same basic unit with a graphite helix heating element in place of the wire wound heater. With this arrangement we will be able to extend these curves and get a better idea of how the thermal conductivity is affected by the various methods developed. An additional change is the incorporation of tungsten 5% rhenium vs. tungsten 20% rhenium thermocouples which will be used in addition to the sight holes for optical measurement. The thermocouples will be located 90° away so as to minimize possible interferences. An

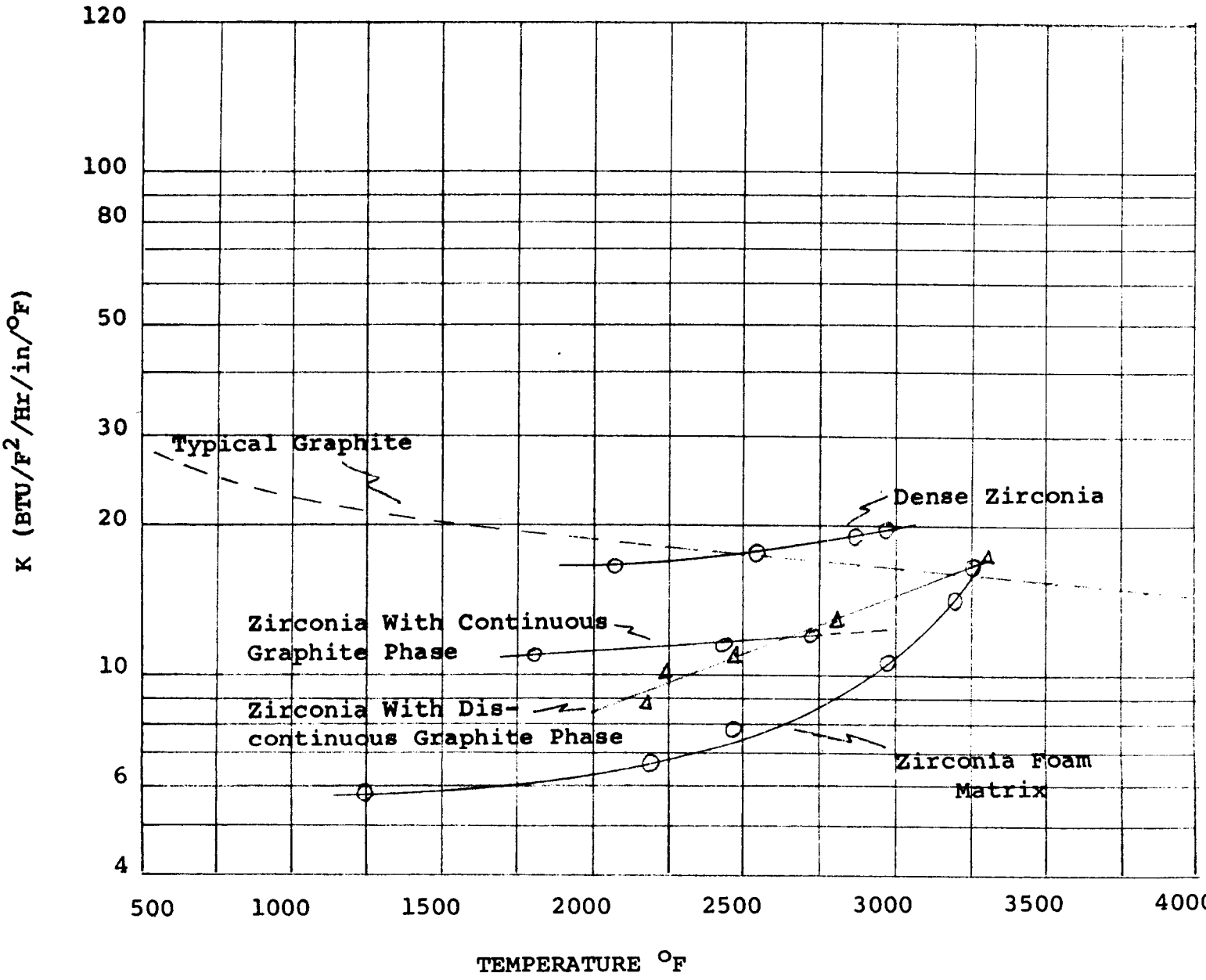


Figure 13
Thermal Conductivity Verses Temperature

advantage of the thermocouple holes is that they will be along isotherms and will less seriously effect the radial temperature gradients. The equipment in its modified form should be capable of thermal conductivity measurements to deep hole temperatures of about 4000°F. Based on our materials evaluations to date this should be sufficient for testing most ceramic foams to the point of severe hot face degradation.

The support of National Aeronautics and Space Administration, Washington, D. C., for the support of this work under Contract NASr-99 is gratefully acknowledged.